

NASA Contractor Report 3849

Thermoplastic/Carbon Fiber Hybrid Yarn

M. E. Ketterer

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FOREWORD

This report was prepared by personnel of Celanese Research Company under contract NAS1-15749, Task Assignment No. 6. This work was administered under the direction of the National Aeronautics and Space Administration, Langley Research Center, Hampton, Virginia.

This report entitled "Modified Composites Fabrication" covers the work period of October 1982 through September 1983. The report was released by the author in January 1984.

Contract Administrator for Celanese was Mr. William D. Timmons, assisted by Jean E. Hileman. Technical Manager was Dr. Alan Buckley, and Research Supervisor was Dr. Morton Glick. Special mention should be made for contributions and efforts put forth during this contract by Dr. Joseph R. Leal, Contract Administrator, Mr. Lincoln Ying, Research Engineer and Mr. Victor Astone, Technician.

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1. SUMMARY:

The rheological behavior of thermoplastic materials inhibits impregnation and "wet out" of carbon fiber bundles. Furthermore, preforms made by hot melt or solution coating of the fiber are usually stiff, brittle and non-drapeable. Under Task Assignment No. 6, efforts were directed to develop processing methods to make CF/TP fiber preforms that are easy to handle and drapeable, and to consolidate them into low void content laminates.

These objectives have been attained with the development of the hybrid yarn concept; whereby, thermoplastic fiber can be intimately intermixed with carbon fiber into a hybrid yarn. This has been demonstrated with the intermixing of Celion® 3000 with: a Celanese liquid crystal polymer fiber, polybutylene terephthalate fiber, or polyetheretherketone fiber. The intermixing of the thermoplastic matrix fiber and the reinforcing carbon fiber gives a preform that can be easily fabricated into laminates with low void content. Mechanical properties of the laminates were not optimized; however, initial results indicate properties typical of a thermoplastic/carbon fiber composite prepared by more conventional methods.

Items delivered under this contract included hybrid yarn samples of polybutylene terephthalate (PBT)/carbon fibers and polyetheretherketone (PEEK)/carbon fibers, and a woven fabric of PBT/carbon fiber.

2. INTRODUCTION:

Thermoplastic (TP) matrix materials for carbon fiber (CF) reinforced composites are of considerable interest for several reasons. CF/TP composites have the potential to offer "tougher" or more impact/fracture resistant composites than their thermoset counterparts. In addition, thermoplastics have essentially

unlimited shelf-life combined with the ability to be rapidly formed since no curing is required. These attributes can potentially combine to offer tougher, lower cost parts with much less extensive capital requirements, e.g., large autoclaves.

There are a number of ways in which the carbon fiber can be combined with a thermoplastic matrix in a suitable preform. Several of these, which include hot-melt and/or solution coating of fiber, lead to stiff, brittle, non-drapeable materials. As a result, the packaging of the continuous product is a problem and its use is limited to simple contour shapes. The rheological behavior of a thermoplastic matrix, however, can lead to inadequate impregnation and wetting in carbon fiber reinforced composites. The high viscosity, low flow characteristic of the thermoplastic melt can be circumvented by forming a hybrid tow of thermoplastic fiber and carbon fiber, which promotes penetration and wetting of the carbon fiber bundle with the thermoplastic matrix. The hybrid yarn concept is adaptable to any continuous filament thermoplastic fiber, and the process produces a drapeable preform suitable for weaving, filament winding or lay-up techniques.

In Task 4, Celanese evaluated various approaches to preparing carbon fiber/thermoplastic fiber preforms. Hybrid fiber preforms were prepared by intermixing yarns of the two types. Although carbon fiber reinforced composites made by fusion of the polybutylene terephthalate (PBT) fibers in the molding operation yielded promising properties, it appeared that more intimate intermingling of individual fibers would yield a superior product form. The objective of Task No. 6 was to develop method(s) of intimately mixing carbon and TP fibers to make hybrid carbon fiber/thermoplastic fiber preforms. Matrix materials evaluated in this Task were a commodity PBT fiber and high performance thermoplastic fibers of polyetheretherketone (PEEK) and a liquid crystal polymer (LCP). Celion carbon fiber was used as the fiber reinforcement.

Carbon and thermoplastic fibers were fed from a creel through an air mixing device to intermingle and uniformly distribute the carbon and incipient matrix fibers. This required spreading individual yarns to widths of several inches, overlaying the opened yarns, and finally condensing the spread yarn to a single hybrid roving. These continuous hybrid rovings were packaged and used as a novel yarn for intermediate product forms.

Laminates were prepared from the LCP/Celion and from the PBT/Celion hybrid yarns for evaluating physical properties of the composites. Due to the limited supply of multifilament PEEK fiber (which was melt spun at Celanese), determination of PEEK/Celion laminate properties was not possible. Processing capability of the PEEK/Celion hybrid yarn into a laminate was demonstrated by the fabrication of a single panel.

One package of PBT/Celion hybrid yarn totalling 1375 meters (513 grams) and one package of PEEK/Celion hybrid yarn of 800 meters (300 grams) were delivered. In addition, one pound of fabric of PBT/Celion hybrid yarn was woven and delivered.

3. EXPERIMENTAL EQUIPMENT AND PROCEDURES:

Task 6 of Contract NAS1-15749 was primarily directed toward process development for preparing an intermixed hybrid yarn with secondary efforts directed toward laminate preparation and evaluation. The hybridization process consists of spreading an untwisted commercial carbon fiber (Celion 3000) and an untwisted thermoplastic yarn with individual (Celanese proprietary) banding jets, and then combining the two yarns such that the result is a well mixed hybrid in a 50/50 fiber volume ratio. The arrangement of the process equipment is dependent upon the nature of the thermoplastic yarn. Examples of different set-ups will be discussed later in this report.

Figure 1 demonstrates the spreading ability of the jet on Celion 3000 carbon fiber and PBT yarn bundles. As shown in Figure 2, the carbon fiber and the thermoplastic yarn are fed to individual banding jets by means of a Godet. The intermixing is imposed by passage of the overlapped and spread fibers through a staggered set of stationary bars, and can be aided by additional guides and rollers. A second godet can be used to minimize yarn tension at the banding jets by slightly overfeeding the yarns from godet #1 to godet #2. The hybrid yarn is collected on a conventional take-up unit. The godet is a driven roll used to forward the fiber bundle for subsequent processing. A smaller idler roll can be used in a skewed alignment to the driven roll, allowing the fiber bundle to be wrapped around the idler and driven rolls with lateral spacing between wraps.

Preparation of the hybrid yarn for laminate fabrication involved making a prepreg layup on a heated mandrel or drum (Figure 3), stacking the required number of plies and spot melting the thermoplastic to maintain the fiber alignment (Figure 4) and compression molding (Figure 5).

To prepare a layup of the hybrid yarn, the mandrel is first wrapped with a release coated Kapton film. The hybrid yarn is then wound onto the rotating mandrel as it is incrementally traversed across the length of the mandrel. Successive wraps of the yarn are laid in close proximity to the preceding wrap with minimal spacing. Once the mandrel is fully covered with a single tier of hybrid yarn, an outer wrapping of the Kapton film is applied. The rotating mandrel is internally heated to melt the thermoplastic. At the same time an external heat gun (if necessary) and manually applied pressure are used to assist in the melting and spreading of the thermoplastic. The resulting fused sheet is then removed without losing fiber alignment. The layup is cut into 3.5" x 10.5" sections (the dimensions of the mold). The Kapton film is removed and the required number of plies are stacked in the mold and spot melted at the edges and the center

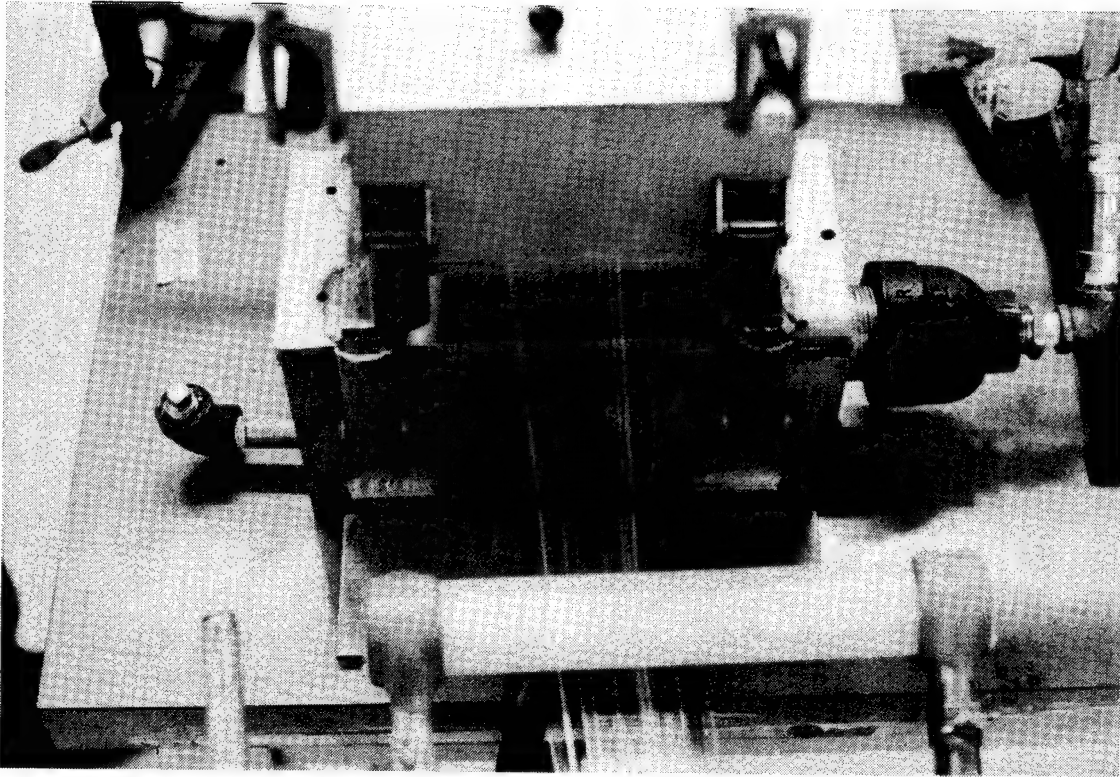


FIGURE 1. PHOTOGRAPH OF PBT (TOP, WHITE) AND OF CELION® (BOTTOM, BLACK) SPREAD BY BANDING JETS

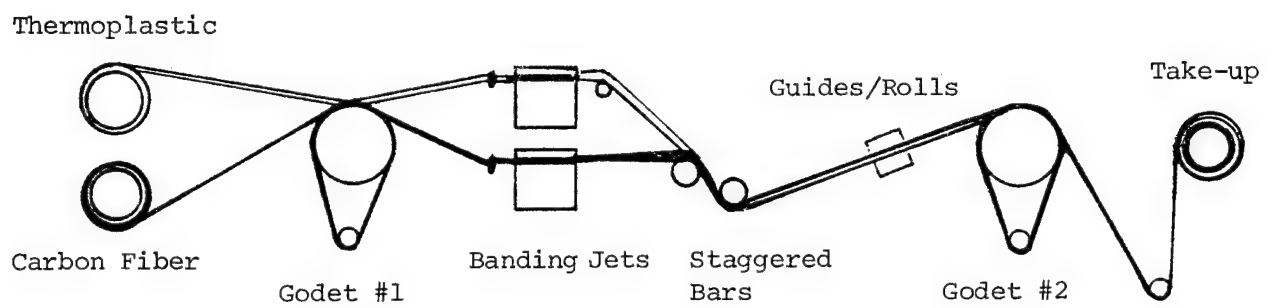


FIGURE 2. SKETCH OF A TYPICAL SET-UP OF HYBRIDIZATION LINE

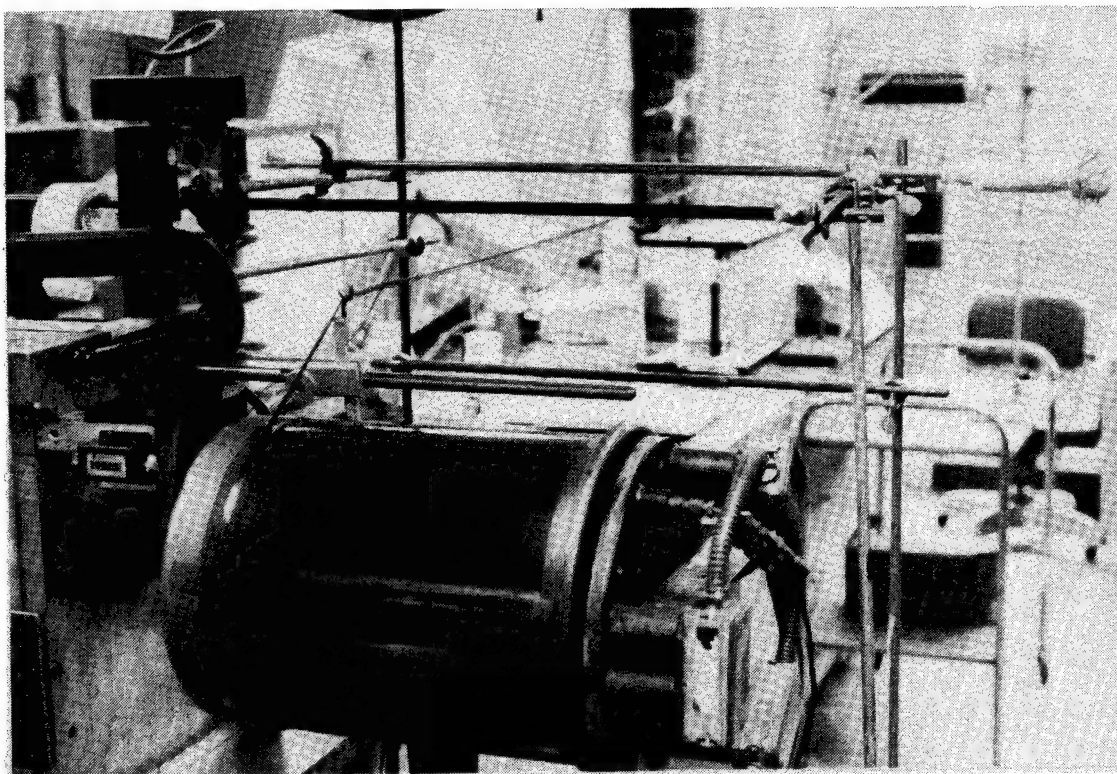


FIGURE 3. PREPARATION OF HYBRID YARN LAY-UP ON A HEATED MANDREL

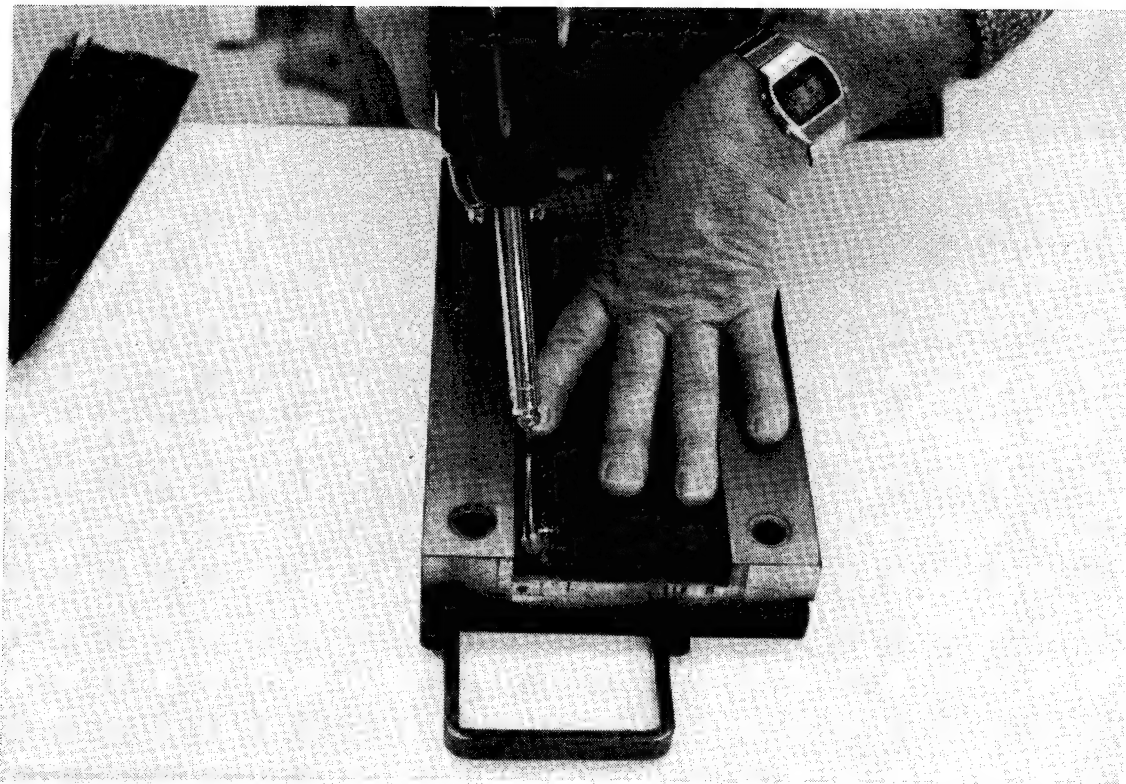


FIGURE 4. STACKING AND SPOT MELTING PLIES IN THE MOLD

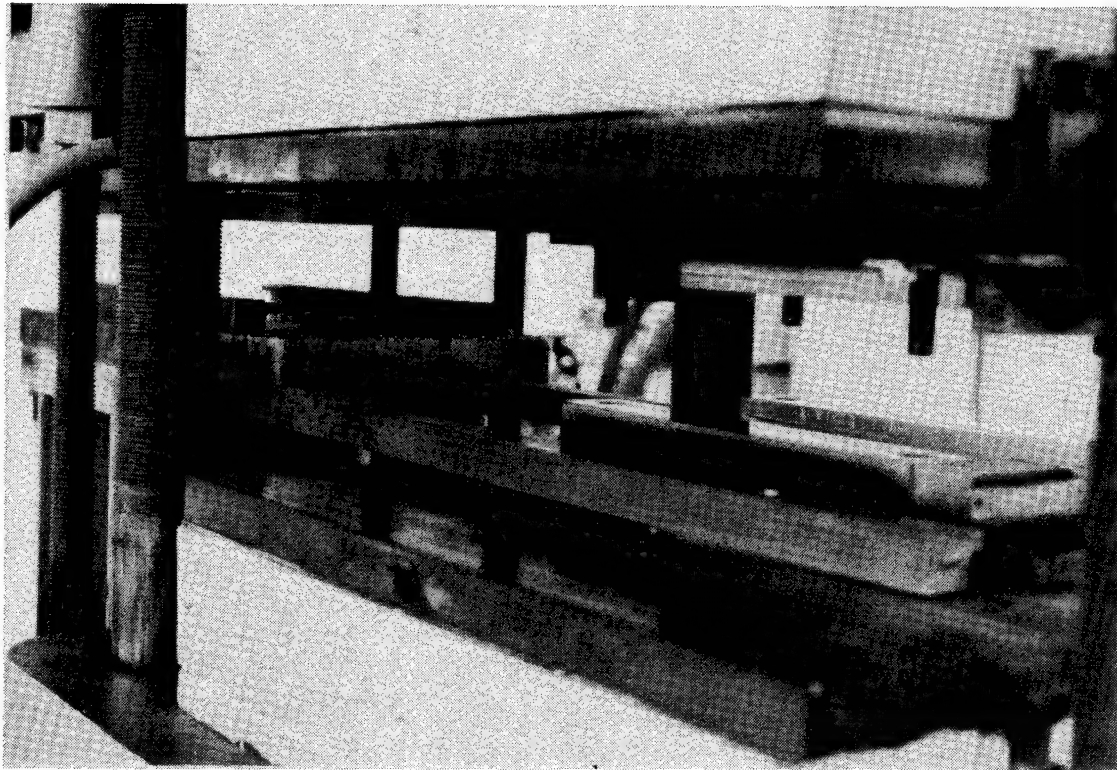


FIGURE 5. HOT PRESS (BACKGROUND) AND COLD PRESS (FOREGROUND)
CONTAINING MOLD AND FINAL PANEL

to retain the alignment of the plies and fibers.¹ To prepare a laminate for tensile testing, eight plies (single layers of hybrid yarn) are used to give a 30 to 40 mil thick panel. For flex and compression tests, 22 plies are used to give an 80 to 100 mil thick panel.

The thermoplastic/carbon fiber composites are prepared by compression molding. A Carver laboratory press is used in conjunction with a 50 ton hydraulic press and a polished 3.5" x 10.5" mold. The Carver press, equipped with heating elements, is preheated to a designated temperature above the melt temperature of the thermoplastic. The mold, containing the stacked plies of hybrid yarn, is then closed with minimal "touch" pressure until the mold heats to the set temperature. This usually takes 2 to 5 minutes, at which time the pressure is raised to a specific molding pressure (200 to 750 psi). Time at set temperature and pressure can vary from 5 to 30 minutes. After the required time in the hot press, the mold is transferred to the cold hydraulic press for cooling to below 140°F.

Specimens prepared for physical testing had a 0° carbon fiber orientation (unidirectional). These panels were cut to size, and properties were determined according to ASTM methods.

4. PBT/CARBON FIBER PROCESS DEVELOPMENT

4.1 PBT/Carbon Fiber Hybrid Yarn

Celion 3000 unsized carbon fibers are mixed with polybutylene terephthalate (PBT) fibers at a 50/50 volume ratio. Stand-

¹ On occasion, an outer wrapping or bag of Kapton film was used to enclose the stacked plies for reasons which will be discussed later.

ard commercial carbon fibers are sized with an epoxy-based finish to enhance handling but are difficult to spread into a uniform monolayer due to the binding effect of the finish. To handle the unsized fibers, extreme care must be exercised to minimize damage to the fiber. An air-banding jet has been identified to be the most appropriate method to spread unsized carbon fibers into a uniform monolayer.

PBT fibers are difficult to process due to their elastic behavior. The elastic properties of the partially drawn PBT prohibit permanent displacement/dispersion within the hybrid bundle. To resolve this problem, the PBT yarn is drawn at a 2 to 1 ratio over a hot shoe; thereby, reducing the elongation from 164% to 28%. Physical properties from single filament tensile tests are listed in Table 1 for PBT, LCP and PEEK fibers. Celion 3000 properties are also included.

Figure 6 is a schematic of the equipment arrangement used for a thermoplastic fiber having a high elongation (i.e., greater than 20%). The PBT yarn supply consists of 17 packages of 33 filaments each of drawn yarn. After passing over godet No. 1, the 17 ends of PBT are kept separate by spreading the ends with a comb. The carbon fiber supply is a single package of Celion 3000, which is fed by godet No. 1 to a banding jet. The PBT and the carbon fiber are overlapped and laced through a comb to blend the two fibers. To minimize tension and stretch on the PBT yarn, a second godet roll is located downstream of the banding jets. The fiber tension is controlled by adjusting the speed of godet No. 1 versus godet No. 2. A set of guides are arranged to produce a gradual twisting of the hybrid yarn prior to the second godet and take-up unit to retain the intermixing. Process speeds range from 7 to 10 m/min.

TABLE 1. PHYSICAL PROPERTIES OF THERMOPLASTIC YARNS EVALUATED AND
CELION 3000 CARBON FIBER

Fiber Type	dpf ¹ (g/9000 m)	Density (g/cc)	Initial Modulus (g/denier)(GPa)	(Msi)	Tenacity (g/denier) (MPa)	(ksi)	Elongation %		
PBT (partially drawn)	5.23	1.35	25.7	3.06	0.444	2.23	266	38.6	164
PBT (drawn)	2.66	1.35	23.6	2.82	0.408	5.31	633	91.8	28
LCP	2.25	1.40	560	69.2	10.0	10.5	1298	188.2	2
PEEK (multi- filament)	36.7	1.30	52.9	6.05	0.880	2.71	309	44.9	66
Celion ² 3000	0.62	1.77	1500	234	34	22.9	3600	520	1.5

- 1 dpf is denier per filament.
- 2 Carbon fiber properties were determined by an impregnated strand test method; while thermoplastic fiber properties were single filament tensile tests.

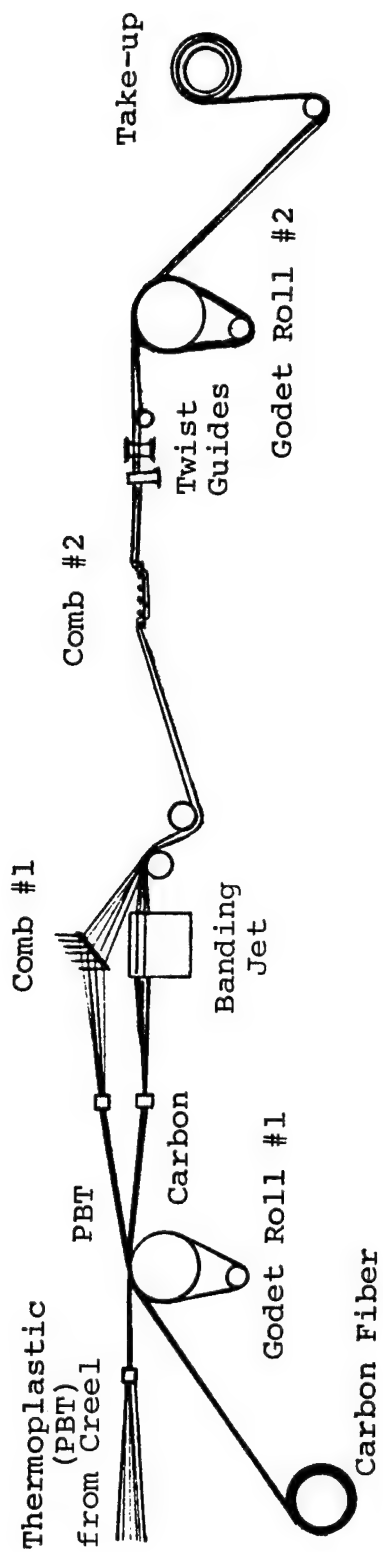


FIGURE 6. SCHEMATIC OF INTERMIXING LINE FOR PBT/CELION® 3000

Laminates from PBT/Celion hybrid were prepared under numerous conditions in an effort to determine parameters for producing panels with acceptable physical properties. Initial efforts resulted in laminates with surface cracks parallel to the fiber direction, and work was directed towards the preparation of crack-free panels. As indicated in Table 2, several sample panels were reprocessed a second or third time to remove surface cracks and/or to increase the carbon fiber volume. Cracks could be avoided by preparing a 0°/90° laminate. Crack free unidirectional panels were ultimately prepared by wrapping the layup in a Kapton film or a Kapton vacuum bag and processing at 750 psi pressure. Previously cracked panels could be repaired by reprocessing in Kapton film at 750 psi. A detailed study to determine the cause of the cracks was beyond the scope of this program.

Table 2 lists the laminates processed and the various molding conditions. Table 3 contains the mechanical properties of the PBT/carbon fiber laminates along with typical properties for a 5208 epoxy carbon fiber composite.

4.2 LIQUID CRYSTAL POLYMER/CARBON FIBER HYBRID YARN:

Developmental liquid crystal polymer fibers produced by Celanese were intermixed with Celion 3000 carbon fiber to make a hybrid yarn preform and laminates. These LCP fibers have an elongation of 2%, which is comparable to the 1.5% elongation of the carbon fiber. Physical properties of LCP and Celion were reported earlier in Table 1. The low elongation of the LCP fiber enhanced the intermixing process and simplified the equipment set-up. Figure 7 is a schematic of the intermixing line used for preparing the LCP/Celion hybrid yarn. LCP fiber was fed from a single supply package of 660 filaments (untwisted) to a godet.

TABLE 2. PBT/CELION® LAMINATE CONDITIONS

OBJECTIVE	TIME at touch		TEMPERATURE T	PRESSURE P	PANEL DESCRIPTION
	pressure	T & P t(2)			
	(min.)	(min.)	(°C)	(°F)	(psi)
1. MINIMUM PRESSURE	10	5	242	(468)	1.4 (200)
					22 PLIES, 3.0mm(.118") THICK, 45% FIBER VOLUME, POOR WETTING OF FIBER
2. ABOVE REPROCESSED	8	20	242	(468)	2.1 (300)
					2.5mm(.102") THICK, 51.6% F.V., CRACKED IN MIDDLE
3. THIN PANEL FOR TENSILE STRENGTH	6	10	242	(468)	2.1 (300)
					8 PLIES, 1.1mm(.044") THICK, 49.5% F.V., SEVERAL CRACKS
4. INCREASED t(2) and T	4	30	244	(471)	2.1 (300)
					8 PLIES, 1.1mm(.045") THICK, TWO CRACKS IN CENTER
5. ABOVE REDONE AT HIGHER P	4	15	244	(471)	3.4 (500)
					1.0mm(.040") THICK, CRACKS STILL IN PANEL
6. ABOVE REPROCESSED 3rd. TIME	5	15	243	(469)	3.4 (500)
					0.9mm(.037") THICK, 61.4% F.V., CRACK STILL IN CENTER OF PANEL
7. HIGH T & P and LONG t(2)	3	30	245	(473)	3.4 (500)
					8 PLIES, 0.8mm(.030") THICK, 63% F.V., CRACKS

(Table 2 continued on next page.)

TABLE 2(cont.). PBT/CELION LAMINATE CONDITIONS

OBJECTIVE	TIME at		TEMPERATURE T	PRESSURE P	PANEL DESCRIPTION
	touch pressure	T & P t(2)			
	(min.)	(min.)	(°C)	(°F)	(MPa) (psi)
8. KAPTON VACUUM BAG, HIGH T&P	3	5	244	(471)	5.2 (750) 8 PLIES, 0.9mm (.036") THICK, 46% F.V., NO CRACKS
9. REPEAT WITH NO KAPTON BAG	3	6	241	(465)	5.2 (750) 8 PLIES, 0.8mm (.032") THICK, 50% F.V., 1 CRACK
10. KAPTON VACUUM BAG	2	5	251	(483)	5.2 (750) 8 PLIES, 0.7mm (.029") THICK, NO CRACKS
11. 0°/90° LAYUP NO KAPTON BAG	3	5	246	(475)	5.2 (750) 8 PLIES, 0.8mm (.032") THICK, NO CRACKS
12. KAPTON VACUUM BAG, 500 psi	3	5	248	(478)	3.4 (500) 8 PLIES, 3 CRACKS
13. 1/2 OF (12) REPROCESSED IN KAPTON WRAP	3	5	247	(477)	5.2 (750) ALL CRACKS REPAIRED
14. 1/2 OF (12) REPROCESSED IN KAPTON VACUUM BAG	3	5	248	(478)	5.2 (750) ALL CRACKS REPAIRED

TABLE 3. PBT/CELION® AND TYPICAL EPOXY/CARBON FIBER COMPOSITE PROPERTIES⁽¹⁾

COMPOSITE	PROPERTY	UNITS	0° FLEX	0° COMPRESSION	0° TENSILE

	FIBER VOLUME (%)		(2) 51.6	(2) 51.6	(3) 49.5 ; (4) 61.4 ; (5) 46.2

PBT/ CELION®	STRENGTH	(MPa)	938 + 34	659 + 83	1517+34 ; 1524+83 ; 1469+48
		(ksi)	(136 + 5)	(96 + 12)	(220+5) ; (221+12); (213+7)
	MODULUS	(GPa)	115 + 2	130 + 8	130 + 5 ; 165 + 4 ; 120 + 3

	FIBER VOLUME (%)		62	62	62

TYPICAL 5208 EPOXY CARBON FIBER	STRENGTH	(MPa)	2000	1517	1724
		(ksi)	(290)	(220)	(250)
	MODULUS	(GPa)	117	117	145

		(Msi)	(17)	(17)	(21)

- (1) Testing done at a room temperature of 23°C (73°F).
- (2) Processed at 242°C (468°F), 1.4MPa (200psi) for 5 min., and 2.1MPa (300psi) for 20 min.
- (3) Processed at 242°C (468°F), 2.1MPa (300psi) for 10 min.
- (4) Processed at 244°C (471°F), 2.1MPa (300psi) for 30 min., 3.4MPa (500psi) for 15 min., and 243°C (469°F) at 3.4MPa (500psi) for 15 min.
- (5) Processed at 244°C (471°F) in a Kapton bag and 5.2MPa (750psi) for 5 min.

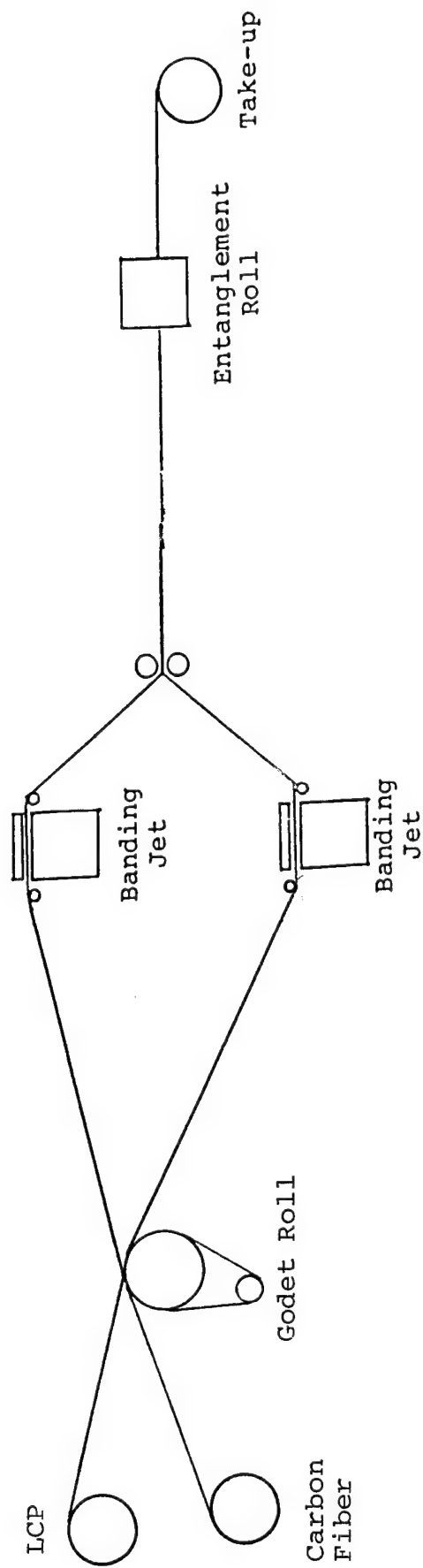


FIGURE 7. SCHEMATIC OF INTERMIXING LINE FOR LCP/CELION®3000

The carbon fiber yarn (untwisted, unsized Celion) was forwarded by the same godet, but separated from the LCP yarn. Each yarn bundle was passed through a separate banding jet, which spread the fiber bundles to a 3 inch span. The spread yarns were overlapped and passed through a set of nip rolls and an entanglement roll to the take-up unit.

Compression molded laminates were fabricated from the LCP/carbon fiber hybrid yarn at 600°F and 500 psi. Time at temperature and pressure was 20 minutes for a 30 to 40 mil panel and 40 minutes for an 80 to 100 mil panel (3.5" x 10.5"). Fiber volumes between 56% and 62% were obtained and microscopic examination of cross sections showed no existence of voids or delamination. Composite properties are listed in Table 4. Problems with surface cracks were not encountered with the fabrication of LCP/carbon fiber panels.

4.3 PEEK/CELION HYBRID YARN:

A 20 pound sample of Victrex® PEEK polymer was melt spun at Celanese into a multifilament fiber. The 10-filament packages were drawn over a hot shoe at a 2 to 1 ratio to give a 380 denier yarn. Physical properties of the PEEK were listed earlier in Table 1. Packages of PEEK were intermixed with carbon fiber on the same process set-up as was used with PBT/carbon fiber intermixing, since PEEK fiber also has a high elongation of 66%.

A single laminate of PEEK/Celion 3000 was prepared to demonstrate processing capability. Kapton film was not used due to its questionable thermal stability at processing temperatures of 710 to 750°F. To insure a crack-free panel, a 0°/90° layup was used. Final pressure was 500 psi in the hot press. Due to the limited supply of multifilament PEEK, composite properties were not determined.

TABLE 4. COMPOSITE PROPERTIES OF LCP/CELION CARBON FIBER

TEST TEMPERATURE	PROPERTY	UNITS	0° FLEX	0° COMPRESSION	0° TENSILE

ROOM TEMPERATURE	FIBER VOLUME	(%)	56.3	56.3 ; 61.4	60.3

	STRENGTH	(MPa)	1262+145	627+48 ; 634+55	1503+34
		(ksi)	(183+21)	(91+7) ; (92+8)	(218+5)
93°C (200°F)	-----				
	MODULUS	(GPa)	105+3	132+8 ; 149+12	128+3
		(Msi)	(15.2+0.4)	(19.1+1.2);(21.6+1.8)	(18.6+0.4)

93°C (200°F)	STRENGTH	(MPa)	538+48	352+41 ; 365+27	-
		(ksi)	(78+7)	(51+6) ; (53+4)	-

	MODULUS	(GPa)	92+3	107+1 ; 121+10	-
		(Msi)	(13.4+0.5)	(15.5+0.1);(17.6+1.4)	-

4.4 WOVEN HYBRID YARN FABRIC:

Weaving of one pound of PBT/Celion hybrid fabric was accomplished after several investigative trials to compact the loose and flared hybrid fiber bundle to be more desirable for fabric weaving. Such attempts as twisting and applying a starch binder were unsuccessful due to the high initial modulus and brittleness of the Celion fiber. Another immediate alternative was to wrap the hybrid bundle with a 100 denier PBT yarn at four wraps per inch to form the compact yarn. This wrapper will then become part of the matrix upon composite fabrication. The wrapped hybrid yarn was equally divided into ninety-six spools and mounted on a special creel for warping of a six-inch-wide fabric weaving on a modified Draper XD loom at Southern Weaving Co., Greenville, SC. Various weave patterns (satin, twill, basket and plain) were investigated for fabric dimensional stability and pliability. As a result, one pound of plain weave fabric (16 EPI x 15 PPI),¹ weighing 16 oz/yd², was produced. The fabric, 35 mils in thickness, was a rather soft but compact fabric with the appearance of well intermingled hybrid yarn. This fabric was delivered to NASA-Langley as well as 1375 meters (513 grams) of PBT/Celion 3000 hybrid yarn and 800 meters (300 grams) of PEEK/Celion hybrid yarn.

1 EPI is warp ends per inch and PPI is picks per inch, where "pick" is one crosswise length of filling yarn, perpendicular to the warp yarn.

5. CONCLUDING REMARKS:

The concept of the hybrid thermoplastic fiber and carbon fiber yarn has all the advantages of more conventional thermoplastic fiber reinforced composites. In addition, the intermixing of the thermoplastic fibers with the carbon fiber (or other fiber reinforcement) offers an improved route to impregnation of the resin into the carbon fiber bundle to produce a low void content in the composite. The hybrid yarn is a handable and drapable material which is readily adaptable to existing preform/composite fabrication processes (e.g., filament winding or woven fabrics), especially those with complex shapes. The concept of producing the hybrid yarn is applicable to any thermoplastic fiber with only minor modifications.

This program has demonstrated the ability to intermix a thermoplastic fiber with a carbon fiber for fabrication of laminates having mechanical properties typical of thermoplastic reinforced composites.

It is recommended that the program should be extended for more in-depth study. Areas of interest are:

1. Evaluation of laminate fabrication parameters and composite properties at various levels of intermixing.
2. Evaluation of fiber sizing for improved wetting of the reinforcing fiber by the thermoplastic and for improved handling of the hybrid yarn during laminate preparation or weaving.
3. Optimization of the intermixing line with regards to developing a commercially applicable process.
4. Optimization of laminate fabrication conditions for consolidation of hybrid yarns into composites.

5. Develop spinning processes for various thermoplastics that are matrix candidates which are not presently available in fiber form.
6. Evaluation of different weave patterns or fabric structures made from hybrid yarn for laminate fabrication and characterization.

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